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METHYL ETHYL KETONE PEROXIDES, RELATIONSHIP OF REACTIVITY TO CHEMICAL STRUCTURE

by
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INTRODUCTION

Of all commercially available organic peroxides, probably more has been written about the behavior of methyl ethyl ketone peroxide in the ambient temperature curing of unsaturated polyester resins than about any other initiator (1). Many avenues of interest have been explored — gel times with varying amounts of cobalt accelerators, effect on that gel time of a variety of inhibitors (2), gel to peak exotherm, hardness development, etc.

Although this staggering amount of documentation is most helpful in determining how a particular MEKP will behave under a variety of conditions, the available literature does little to explain why it behaves so.

The purpose of this paper is to attempt, at least partially, to fill this void. It will be made apparent that the various reaction products of methyl ethyl ketone and hydrogen peroxide greatly affect the parameters of gel and cure in polyester and vinyl ester resins. Since commercially available MEKP's contain a mixture of these reaction products, in varying proportions, dependent on the manufacturer, on the production conditions when made and the length of storage, the actual behavior of the MEKP can be predicted once the component ingredients are known.

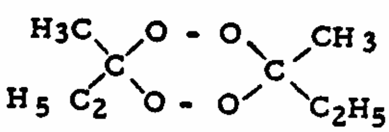
In addition, active oxygen and percentage MEKP will be discussed.

HISTORY

As far as can be determined, the earliest mention of methyl ethyl ketone peroxide was in the German publication Berichte, in 1899, by Baeyer and Villiger who were experimenting with Caro's acid and various ketones (including methyl ethyl ketone) (3).

It was not until 1936 and 1937 that the first patents appeared for the manufacture of methyl ethyl ketone peroxide (4).

Methyl ethyl ketone peroxide made its debut into the U.S. marketplace in 1949 (5). It was quite normal for these early commercial MEKP's to gas and have horrendous activity changes on storage. It was thought that the empirical formula for MEKP was as follows (6):



It was based on this empirical formula that early active oxygen contents and peroxide percentages were derived, quite erroneously as we now know. Our present day knowledge also leads us to believe that the product depicted by this particular structural formula is not produced.

To further complicate matters Karnojitski proposed that a variety of other compounds were present following the reaction of MEK with hydrogen peroxide (7). The structural formulae of these proposed compounds are shown in table 1.

But Karnojitski was in many ways correct. Commercially available MEKP's are not simple substances, as will be seen when the reaction possibilities are investigated.

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MANUFACTURE

Methyl ethyl ketone peroxide is produced by the reaction of methyl ethyl ketone and hydrogen peroxide under acidic conditions. Due to the hazards involved in producing the pure forms of MEKP, commercial manufacture of methyl ethyl ketone peroxide is always carried out in the presence of phlegmatizers or plasticizers.

It is well known that commercial methyl ethyl ketone peroxide formulations are mixtures of several species of peroxides existing in equilibrium. Table 2 illustrates the myriad of ketone peroxide structures that could form under various conditions.

The reaction between hydrogen peroxide and methyl ethyl ketone is conducted in an acidic environment. The degree of acidity, reaction temperature and reaction time determine what species of peroxides are formed and to what extent. After their initial formation, the various structures begin to equilibrate to their most stable configuration, the rate of which is also dependent on pH and temperature.

While Table 2 may seem to have introduced as much complication as the proposals of Karnojitski, rescue comes from the phenomenon of dissociation. Through the work of Antonovski it is known that some of the reaction products of MEK and hydrogen peroxide will dissociate in solution (8). Since all commercial MEKP's are prepared and sold in solution, dissociation reduces the number of compounds available for reaction as shown in table 3.

Table 3 defines the structures which are subject to this discussion. Table 4 shows the variety of peroxide species with their theoretical active oxygen content. Type O and type 1 are unstable precursors existing in theory. They were not isolated. They can exist at neutral conditions but immediately react in acid media to form type 2 and type 4 which are in equilibrium with each other. This equilibrium favors type 4 in solutions containing hydrogen peroxide. The net result of these reactions is that type 4 is the principal initial component formed in MEK peroxide formulations. Type 4, however, slowly shifts to its dimer-type 3 plus hydrogen peroxide under acid conditions at ambient temperature.

Thus, a commercial product must be adequately neutralized immediately after manufacture to prevent this gradual but constant shift of type 4 to type 3 peroxide.

It is not within the scope of this paper to define what adequate neutralization is, but if not properly neutralized, commercial MEK peroxide formulations will continue to re-equilibrate, or drift, while in use or in storage. This contributes to processing problems for users of MEK peroxides.

Each MEK peroxidic component has individual reactivity characteristics - that is, the rate at which it reacts to cobalt activators, and therefore the rate at which it initiates copolymerization of styrene and unsaturated polyester resin at ambient and elevated temperatures. Therefore, if an MEK peroxide is undergoing re-equilibration while in use or in storage, its reactivity will also be undergoing change. The result to the fabricator will be unpredictability in curing unsaturated polyester parts. Gel and cure times can vary for a single lot of MEK peroxide with time, and equally serious, gel and cure times can vary from lot to lot, causing problems on the production floor.

BEHAVIOR IN POLYESTER RESIN

It can be seen from the above that the peroxide types available for reaction in a cobalt accelerated polyester resin would be Type 4, (2, 2-di hydroperoxy butane), its dimer, Type 3, (2,2'-di hydroperoxy -

2,2'-di-n-butyl peroxide) and the cyclic and polymeric peroxygen compounds. However, it was been found that the cyclic and polymeric products are inert with cobalt at ambient temperatures and thus have no influence on the gel and cure of the unsaturated polyester resin. They do however contribute to the total active oxygen content.

In all commercial MEKP's, a small amount of hydrogen peroxide remains as a reaction residual. In some formulations hydrogen peroxide is added to give a faster gel. Since hydrogen peroxide reacts with the cobalt carboxylate accelerators in the polyester resin, the reaction parameters of hydrogen peroxide must also be taken into consideration.

Thus the behavior of commercial methyl ethyl ketone peroxides in the gelation and cure of cobalt accelerated unsaturated polyester resins is dependent upon the presence and amount of hydrogen peroxide, type 4 MEKP and type 3 MEKP.

ACTIVE OXYGEN

Since MEKP is sold having a certain "total active oxygen content" it should be understood what is meant by total active oxygen. On a molecular weight basis, if the organic peroxide R-O-O-R has a molecular weight of 100 and the extra oxygen atom a molecular weight of 16 the active oxygen content would $\frac{16}{100}$ or 16% of active oxygen.

Most commercial MEKP's of the "60%" concentration contain between 10% and 11% total active oxygen. However, as all the peroxygen linkages present in the solution contribute to this active oxygen content, and as will be seen these various peroxygen compounds behave differently in polyester and vinyl ester resins, active oxygen content as a measure of activity is erroneous. For example a 23% solution of hydrogen peroxide which would contain approximately 11% active oxygen could hardly be considered a replacement for MEK peroxides in curing polyester.

Also the percentage concentration of MEKP, often depicted as 60%, is misleading. No commercial MEKP contains 60% of methyl ethyl ketone peroxide. As has previously been stated the activity of MEKP in the cure of polyester resins is dependent on the content of type 4 and type 3 MEKP together with hydrogen peroxide. Of the two reactive MEKPs, type 3 has the lowest active oxygen content - 22.86%. A solution of type 3 MEKP at 11% active oxygen would only be about 48% concentration.

Thus, an analysis of commercial methyl ethyl ketone peroxides shows that they contain slightly over 40% of usable peroxide compounds, and as this paper will demonstrate, it is not the active oxygen content, nor the percentage concentration of the solution which determine the activity of the commercial methyl ethyl ketone peroxide formulation in the resin, but the relative amounts of type 4 MEKP, type 3 MEKP and hydrogen peroxide.

The purpose of this study was to investigate the separate action of these three peroxygen compounds in commercially available polyester and vinyl ester resins, and to relate these findings to commercially available methyl ethyl ketone peroxide formulations. The activity changes with time, resulting from shifts in the concentrations of type 4, type 3 and free hydrogen peroxide, were also studied in some of these commercial MEKP formulations.

PROCEDURE

Samples of the leading commercial MEKP peroxides were analyzed for total active oxygen, hydrogen peroxide, type 4 and type 3 peroxide content. In addition, type 4 and type 3 peroxides were synthesized in as pure a solution as possible. Results are summarized in Table 5. Control samples of all the initiators used, including the synthesized type 3 and type 4, were stored at 5°C to maintain as constant an equilibrium balance as possible. These control samples were used to obtain the initial gel and cure parameters for the resins used.

Several initiators were stored at 25°C (77°F) for six weeks, re-analyzed to determine whether composition had changed or equilibrium had shifted. These initiators were then used to cure several of the resins to illustrate how cure parameters depend on initiator composition.

The resins chosen for this study are readily available commercial polyester and vinyl ester resins. The characteristics of these resins were as follows:

Resins

Resin 1 Unsaturated polyester, prepromoted, corrosion resistant, low viscosity, fire retardant laminating resin.

Resin 2 Propoxylated bisphenol A fumarate polyester, prepromoted, corrosion resistant.

Resin 3 Unpromoted isophthalic polyester mildly corrosion resistant.

Resin 4 Vinyl ester, corrosion resistant, unpromoted, (Promoted with 0.5% cobalt naphthenate, 6%, plus 0.05% DMA.)

Resin 5 General purpose unpromoted polyester, phthalic-maleic.

Resin 6 General purpose unpromoted polyester, isophthalic-maleic.

Resin 7 Propromoted polyester, medium viscosity, casting and marble resin.

APPLICATION TESTS CARRIED OUT:

The following application tests were conducted:

a. Gel time - on the Sunshine Gel-Time meter, the time to gel 40 grams of the polyester catalyzed with 1% by weight of the peroxide, at 25°C.

b. Time to peak - the time to reach peak exotherm. After gel time, a thermocouple is placed in the resin sample and the exotherm temperature recorded. Time to Peak is the total time from addition of the peroxide to maximum exotherm temperature.

c. Peak Temperature - the maximum exotherm temperature attained.

d. Barcol Hardness - determined with the Barber-Coleman impressometer, one hour after peak exotherm, and at various time intervals thereafter to measure hardness development.

DISCUSSION OF RESULTS

Portions of all the initiators studied were stored refrigerated at 5°C to preserve their activity and stability. Analytical and test data compiled at this temperature serve as a basis for comparison of change expected to occur at ambient and elevated temperature storage, and also to illustrate differences in activity which are attributable to resin/promotor drift, which otherwise would be obscured by other factors.

By comparing the analytical composition of the peroxides with cure performance in the resin, insight was gained regarding the role that the various initiator components play in the cure process.

Figures 1 to 8 are exotherm curves of temperature versus time for several MEK peroxides in various commercial resins. All cures were measured at 25°C. (77°F) in air. Corresponding data are shown in tables 6 to 13.

Resin 1, Fire Retardant.

Get times ranged from 8 to 15 minutes with commercial ketone peroxides (reference Table 6), and cure times from 26 to 33 minutes. Activity of this resin is controlled by hydrogen peroxide and Type 4 content. Type 3 peroxide required over two hours to gel this resin. Cures by all commercial peroxides were similar, with MEKP A gelling, and reaching maximum exotherm in less time due to its higher hydrogen peroxide level. See figure 1 for exotherm curves.

Resin 2, Bisphenol A.

Gel and cure times were longer in this resin, ranging from 34 to 55 minutes to gel and 51 to 70 minutes to cure with commercial products. Type 4 MEKP plays the dominant role, assisted by hydrogen peroxide to speed gel times. The formulation of pure Type 3, lowest in type 4 concentration and also low in hydrogen peroxide was the slowest, requiring over 3 hours to gel this resin. Initiator D-2 was slower than another lot D-1, because of its lower concentration of type 4 MEKP and H_2O_2. Figure 2 and table 7 summarize cure data. Figure 2A illustrates that there was no significant change in cure of this resin after allowing the MEKP formulations to stand at 25°C for 6 weeks.

Resin 3 - Isophthalic

This mildly corrosion resistant resin is cured by type 4 ketone peroxide, as was resin 2. Cure rate is proportional to type 4 content, with hydrogen peroxide having no influence. Type 3 ketone peroxide alone cured very slowly, requiring over 3 hours to gel and cure. See figure 3 and table 8.

Resin 4 - Vinyl Ester

Figure 4 and table 9 illustrate the difference in the cure of this resin compared to the unsaturated polyester resins. Type 3 methyl ethyl ketone peroxide cures vinyl ester resins, while type 4 does not. Gel times, cure times and peak exotherms are proportional to type 3 content in the initiator formulation. The greater the type 3 content, the faster the gel, the faster the cure and the higher the peak exotherm attained.

Those formulations containing at least 10% type 3, or having isomer ratios less than about 2.5 gelled in about 30 minutes, cured in about 60 minutes and developed Barcol hardness. The others failed to develop Barcol hardness within 25 hours. The two lots of initiator D showed a wide variation in performance in this resin, due to the fact that D-2 had twice as much type 3 as D-1. MEKP C, having the highest concentration of MEKP type 3 cures the fastest of the commercial peroxide formulations.

After 6 weeks storage at 25°C, the compositions and therefore the activities of all the MEK peroxides formulations had undergone some change, as illustrated by comparing figures 4 and 5, and tables 5 and 11. Commercial formulation D-2 increased in type 3 isomer content from 15 to 22% resulting in a decrease in cure time of about 6 minutes. Type 4 MEKP formulation also shifted in composition to form 11.6% Type 3 MEKP so its gel and cure times also decreased appreciably.

Resin 5 - G.P., Phthalic-Maleic

The cure of this general purpose polyester resin was dependent on both the Type 4 isomer and hydrogen peroxide content of the initiator. MEKP A gelled and cured faster than pure type 4 due to the former having a slightly higher H_2O_2 content. See figure 6 and table 12. Peroxide formulations low in type 4 cured well if they contained sufficient hydrogen peroxide. After 7 weeks storage at 25°C, all initiators cured slower.

Resin 6 - B.P. Isophthalic - Maleic

Gels and cures were proportional to type 4 concentration. (See figure 7). Hydrogen peroxide concentration was not a significant factor.

Resin 7 - Casting, Marble

This resin responds to type 4 peroxide and hydrogen peroxide. Type 3 required about 4 hours for gelation. Hydrogen peroxide assisted in gel and cure in those formulations high in type 3 ketone peroxide. (See figure 8 and table B).

CONCLUSIONS

Commercial methyl ethyl ketone peroxide solutions are composed of three peroxide species useful for the curing of cobalt accelerated unsaturated polyester and vinyl ester resins. The three components are: 2, 2-di hydroperoxy butane, 2, 2'-di hydroperoxy-2,2'-di-n-butyl peroxide, and hydrogen peroxide. These active ingredients exist in a delicate equilibrium in commercial formulations.

There are often variations in the concentrations of these active species in commercial methyl ethyl ketone peroxides because of:

Inadequately controlled manufacturing conditions resulting in varying amounts of the three active ingredients from batch to batch. Insufficient neutralization of the post reaction mixture which causes equilibrium shifts during storage.

Prolonged elevated temperature storage also causes equilibrium shifts, especially noticeable where little control has been applied to the manufacturing process.

It has been demonstrated that the three active species make widely differing contributions to the gel and cure of polyester and vinyl ester resins. Also that the behavior of commercial MEKP in polyester and vinyl ester resins is dependent upon the amounts of these three active ingredients present in the solution. Variations in the proportions present of the three species lead to variations in gelation and cure causing production problems for fabricators. Consistency in the amounts of type 4 MEKP, type 3 MEKP and hydrogen peroxide content are the best measure of consistent performance for MEKP.

Active oxygen content is no criterion of MEKP quality. It is merely a measure of the total amount of peroxide present, and is no measure of the performance in any given system.

Commercial MEKPs do not contain "60%" methyl ethyl ketone peroxide. The figure 60% was derived from antiquated and erroneous premises which have not been changed by the majority of suppliers.

All resins currently known as unsaturated polyesters i.e., the condensation product of di basic acids and polyglycols in a monomer solution, are cured, in the presence of a cobalt carboxylate, by the action of 2, 2-di hydroperoxy butane (type 4 MEKP) and to a lesser extent by 2, 2' di hydroperoxy -2, 2' di-n-butyl peroxide (type 3 MEKP). Gelation is augmented by the presence of hydrogen peroxide.

For the class of resins known as vinyl esters, gelation and cure is dependent on the presence and amount of type 3 MEKP. The higher the amount of type 3 present, the faster the gel and cure. Type 4 MEKP gives very inferior results and hydrogen peroxide does not contribute at all to the gelation and/or cure. (10).

REFERENCES

1. Rees, D.E., Long, F.A., McCloskey, C.M. Paper presented at the 31st Annual Meeting of the Reinforced Plastics Division, Society of the Plastics Industry, Washington, D.C., 1976.

2. Kolczynski, J.R. et al, Paper presented at the 22nd Annual Meeting of the Reinforced Plastics Division, Society of the Plastics Industry, Washington, D.C. 1967.

3. Baeyer and Villiger, Berichte 32, 3625 (1899).

4. British patent 44, 544, March 23, 1976. U.S. Patent 2,092,322, September 7, 1937.

5. Rybolt, C., and Swiggert, T., Modern Plastics, 26, April 1949.

6. Cywinski, J.W., "The Role of Organic Peroxide is Curing Polyester Resins and Their Influence on the Physical Properties of Reinforced Plastics" -Novadel, London 1960.

7. Karnojitzki, V., Les Peroxydes Organiques, Paris, 1958.

8. Antonovski, V.L. and Terentjev, V.A., Zhurn, Fiz, Khim 39 621, 2901 (1965).

9. Williemse, F.R.J., Polymeri, Moscow, 1974.

10. U.S. Patent 3,980,731.

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James R. Kolczynski, Manager, Research and Development, Noury Chemical Corp., Burt, N.Y. Graduate of the University of Buffalo, B.A.; M.A.; Associated with Becco Chemical Div., FMC Corporation and Lucidol Div., prior to joining Noury Chemical Corp. in 1974. Publications and patents in fields of free radical polymerization, inorganic and organic peroxides and their applications.

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Product Manager, Noury Chemical Corporation, has been engaged in development and technical service for the unsaturated polyester industry since 1963. Studied polymer chemistry and technology at John Dalton College of technology Manchester and Leicester College of Technology, Leicester (England). Before joining Noury Chemical Corporation in 1974 he has held a variety of technical positions in the organic peroxide field with Noury associates in England and Italy since 1967.

TABLE 1

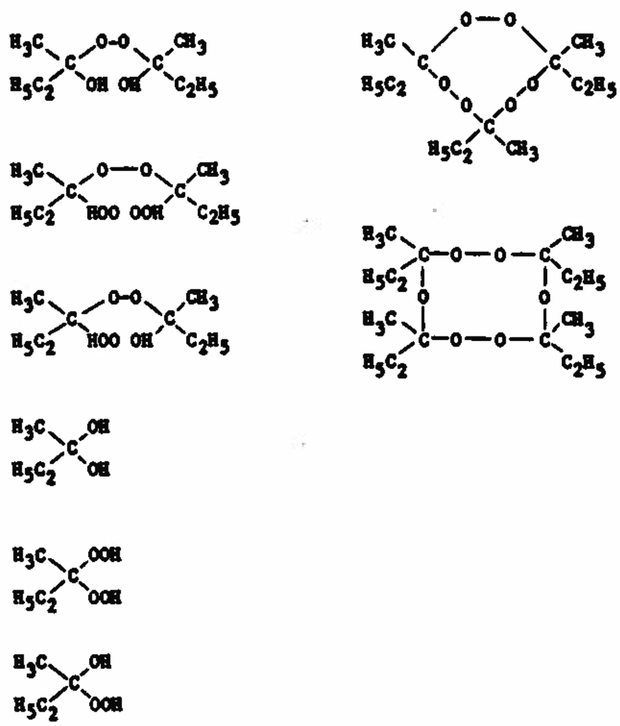


TABLE 2

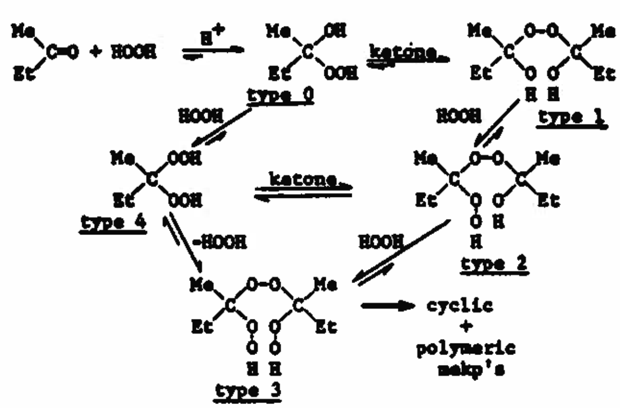


Table 3

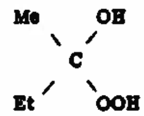
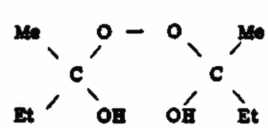
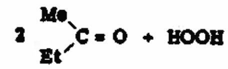
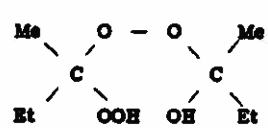
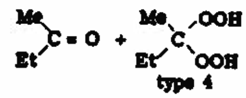
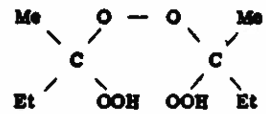
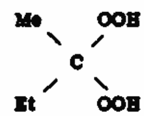
Type	Structure		Result
Type 0			not stable at 20°C
Type 1		—>	
Type 2		—>	
Type 3		—>	relatively stable
Type 4		—>	" "
cyclic and polymeric peroxides		—>	stable

Table 4

Methyl Ethyl Ketone Peroxides

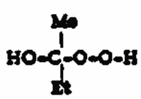
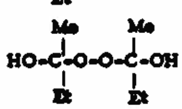
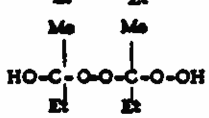
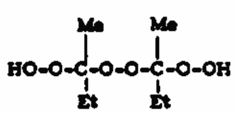
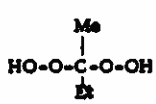
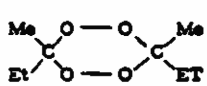
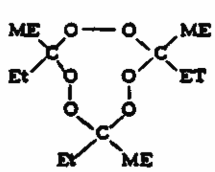
Type	Structure	Chemical Name	Mol. weight	Active Oxygen content w/w %
O		2-hydroxy-2-hydroperoxy butane	106	15.09
1		2, 2'-dihydroxy-2, 2'-dibutyl-peroxide	178	8.99
2		2-hydroxy-2'hydro-peroxy-2, 2'-dibutyl peroxide	194	16.49
3		2, 2'-dihydroperoxy-2, 2'-dibutyl peroxide	210	22.86
4		2, 2-dihydroperoxy butane	122	26.23
Cylic dimer		3, 6-dimethyl-3, 6-diethyl-1, 2, 4, 5-tetraoxacyclo-hexane	176	18.18
Cyclic Trimer		3, 6, 9-trimethyl-3, 6, 9-triethyl-1, 2, 4, 5, 7, 8-hexaoxacyclononane	264	18.18

Table 5

Initial Composition of Methyl Ethyl Ketone Peroxides

MEKP	% Active Oxygen	% H_2O_2	% Type 4	% Type 3	Ratio of type 4: type 3
MEKP A	10.6	2.8	26.5	10.3	2.6:1
MEKP B	10.9	1.7	24.9	15.7	1.6:1
MEKP C	10.4	1.1	21.8	18.2	1.2:1
MEKP D-1	11.1	0.8	33.6	8.4	4.0:1
MEKP D-2	11.0	0.7	27.1	15.5	1.8:1
MEKP Type 4	10.7	0.8	37.7	1.8	20.1:1
MEKP Type 3	10.7	0	2.7	43.7	0.06:1
H_2O_2	10.3	21.9			

Table 6

Cure Characteristics of Various MEK Peroxides in Fire Retardant Resin

MEKP	Gel Time min.	Cure Time min.	Peak Ex. °C
MEKP A	8.0	26.5	153
MEKP B	9.6	29.0	156
MEKP C	11.2	31.2	159
MEKP D-1	12.9	31.9	156
MEKP D-2	14.6	32.5	156
MEKP Type 4	8.8	27.3	150
MEKP Type 3	132	--	--
H_2O_2	92		

Table 7

Cure Characteristics of Various MEK Peroxides in Bisphenol Resin

MEKP	Gel Time min.	Cure Time min.	Peak Ex. °C
MEKP A	37.1	54.0	129
MEKP B	36.8	51.3	136
MEKP C	55.1	69.8	135
MEKP D-1	37.4	53.0	136
MEKP D-2	44.5	60.1	135
MEKP Type 4	34.2	51.5	125
MEKP Type 3	213	230	120
H_2O_2	No gel after 3 hours		

Table 8

Cure Characteristics of Various MEK Peroxides in Isophthalic Resin

MEKP	Gel Time min.	Cure Time min.	Peak Ex. °C
MEKP A	19.6	34.3	157
MEKP C	27.5	43.6	160
MEKP Type 4	16.5	30.2	150
MEKP Type 3	191.0	212.0	167
H_2O_2	No gel after 16 hours		

Table 9

Cure Characteristics of Various MEK Peroxides in Vinyl Ester Resin

MEKP	Gel Time Min.	Cure Time Min.	Peak Ex. °C.
MEKP A	34	62	80
MEKP C	25	45.	119
MEKP D-1	35	73	53
MEKP D-2	25	50	93
MEKP Type 4	63	135	37
MEKP Type 3	11	21	156
H_2O_2	No gel after 16 hours		

Table 10

Cure Characteristics of Various MEK Peroxides* in Vinyl Ester Resin

	Gel Time min.	Cure Time min.	Peak Ex. °C
MEKP A	26.7	50.3	112
MEKP B	34.5	62.0	94
MEKP C	22.9	48.6	126
MEKP D-1	27.5	61.0	65
MEKP D-2	24.1	44.3	114
MEKP Type 4	29.3	52.0	113
MEKP Type 3	13.1	23.1	148

* After storage of initiators at 25°C for 6 weeks.

Table 11

Composition of MEK Peroxides after Storage

MEKP	% Active Oxygen	% H_2O_2	% Type 4	% Type 3
MEKP A	10.6	2.4	26.1	11.1
MEKP B	9.8	3.0	20.5	13.2
MEKP C	10.4	1.2	20.4	19.8
MEKP D-1	11.2	1.1	31.4	10.6
MEKP D-2	11.0	1.0	20.8	22.2
MEKP Type 4	10.4	3.0	24.3	11.6
MEKP Type 3	10.7	0	1.5	45.0

Storage conditions: 25° for 7 weeks

Table 12

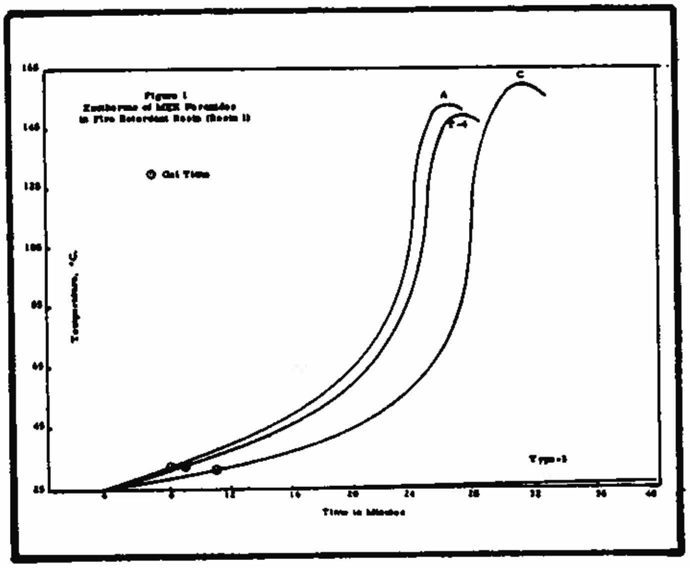
Cure Characteristics of Various MEK Peroxides in General Purpose, Phthalic/Maleic Resin

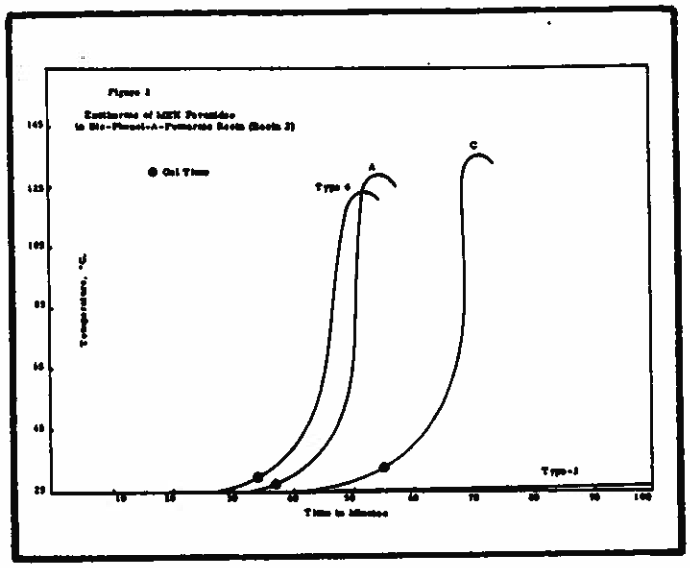
MEKP	Gel Time Min.	Cure Time Min.	Peak Ex., °C
MEKP A	14	27	149
MEKP B	20	34	150
MEKP C	28	43	149
MEKP D-1	21	33	157
MEKP D-2	27	39	155
MEKP Type 4	22	34	150
MEKP Type 3	194	237	135
H_2O_2	20		

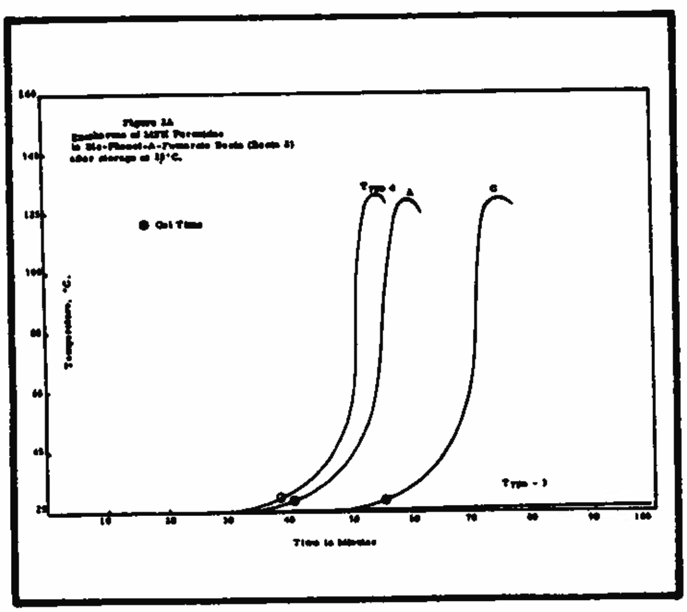
Table 13

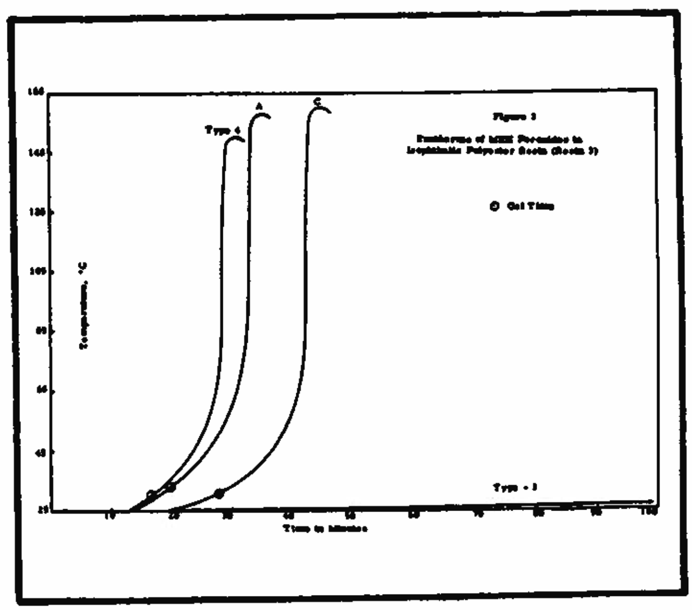
Cure Characteristics of Various MEK Peroxides in Casting Resin

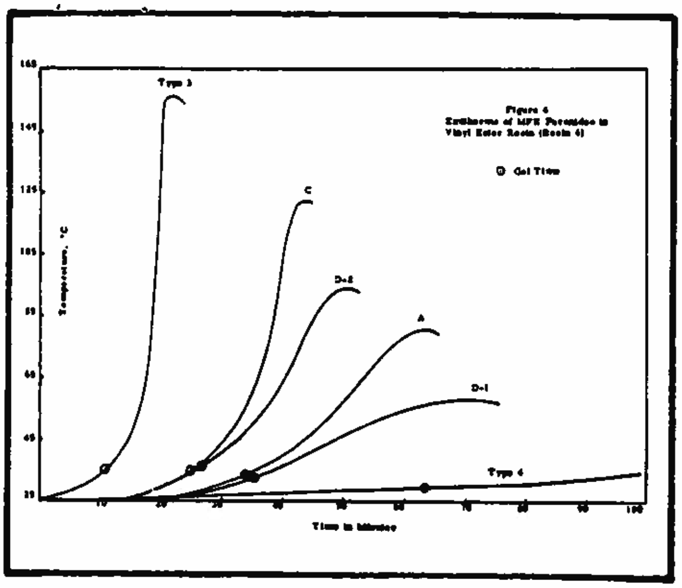
MEKP	Gel Time Min.	Cure Time Min.	Peak Ex. °C
MEKP A	24	44	102
MEKP B	30	52	101
MEKP C	34	54	97
MEKP D-1	35	54	104
MEKP D-2	39	56	102
MEKP Type 4	32	48	107
MEKP Type 3	235	295	33
H_2O_2	23		

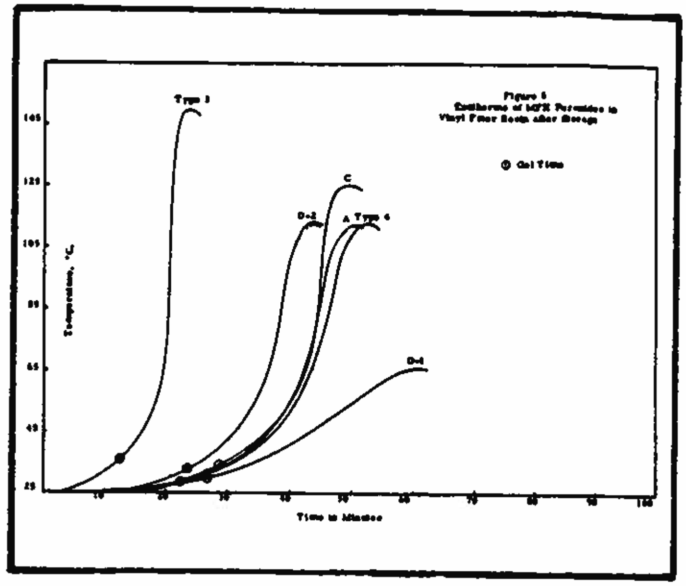


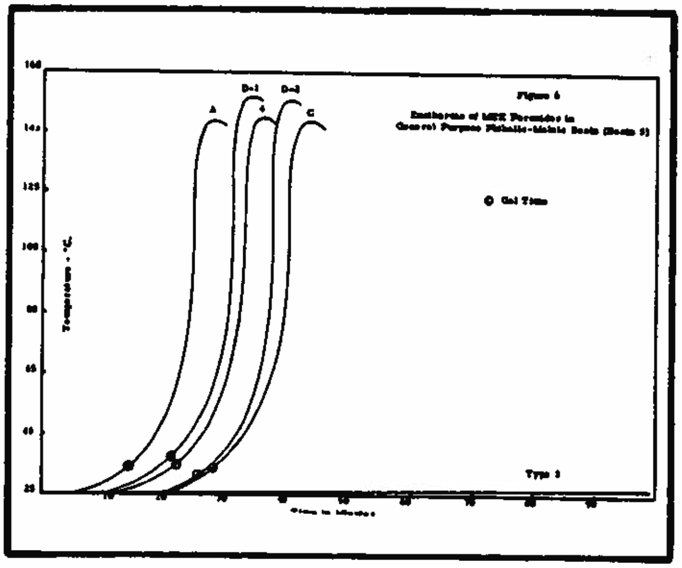


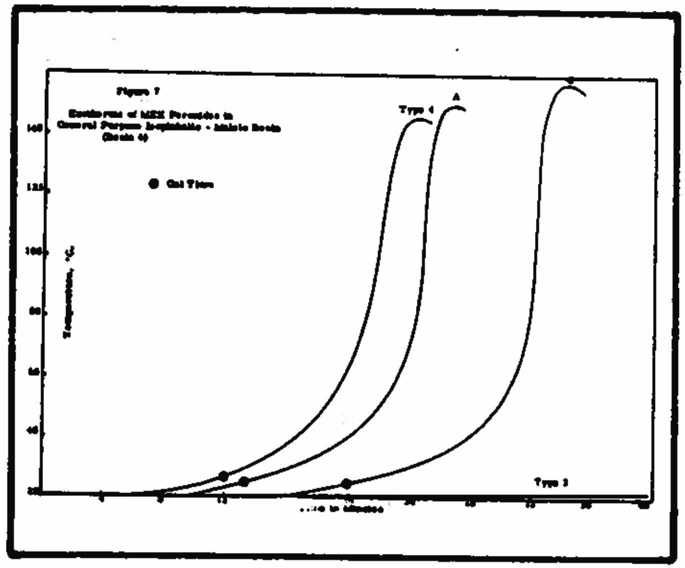


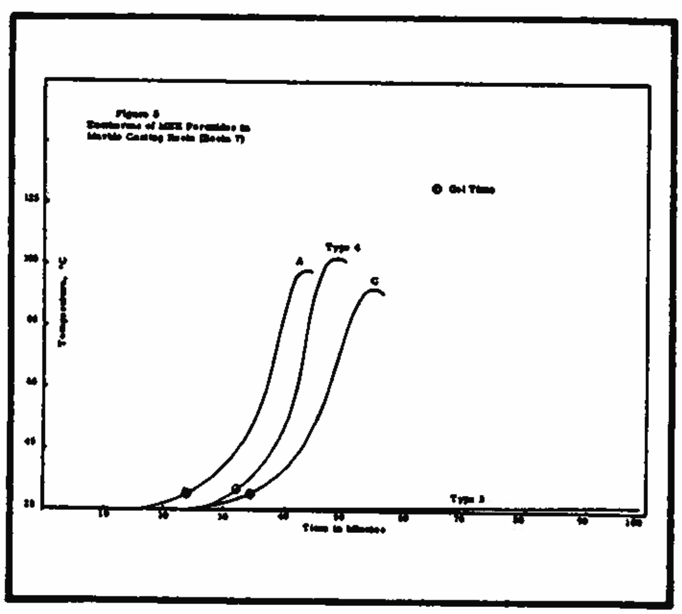



Type 3
C
D-2
A
D-1
Type 4


Type 3
C
D-2
A
Type 4
D-1


A
D-1
4
D-2
C
Type 3


Type 4
A
Type 3


A
Type 4
C
Type 3

half life time / temperature curves for organic peroxides and azo-compounds